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PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

A Process for the Production of Foam from Polymers and/or Copolymers of Vinyl Chloride

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ, N.V., a Company organised under the laws of the Netherlands, of 30 Carel van Bylandtlaan. The Hague Holland, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

For a fairly long time rods and tubes have been produced from diverse thermoplasts by means of suitable extruders. In a conventional continuously operating type of extruder the polymer is pushed by means of a worm-screw through a cylindrical space to a suitable discharge orifice (extrusion orifice) at the end of this space. The polymer is introduced into the apparatus at the other end in a finely divided solid form. The friction caused by the rotating screw usually generates sufficient heat to melt the polymer. Once the molten mass has become homogeneous on further movement through the cylindrical space the extrusion takes place. Polyvinyl chloride is also processed by such a process, although this material's tendency to split off hydrogen chloride on being heated necessitates a very careful control of temperature and duration of heating. Rods and tubes from foamed thermoplasts have also been produced in the continuously operating single shaft extruders which correspond essentially with the apparatuses described above. At the point where the polymer has already melted in the cylinder a volatile liquid, known as a blowing agent, is then added which agent must be homogeneously mixed with the molten polymer in the further movement through the cylinder. The expansion which occurs when the mixtures leaves the extrusion orifice causes

the liquid to evaporate and changes the polymer into foam.

This method of preparing foam has been employed in processing polyolefins and polystyrene, but up till the present time has been considered to be impracticable with polyvinyl chloride. At temperatures above the softening point this material changes into an extremely tough mass which is very difficult to mix with the liquid blowing agent. As a result of incomplete mixing arising from irregular distribution of the forming vapours a poor quality foam is obtained. It is thus necessary to effect the mixing by means of an intensive and comparatively long mechanical treatment, and this polyvinyl chloride cannot tolerate on account of its low thermal stability.

In order to facilitate the homogenization use has been made of plasticizing solvents. However, the removal of these solvents after formation of the foam was very time-consuming and never complete, so that the properties of the polymer were altered by the solvent.

On the other hand, attempts have been made to replace polyvinyl chloride by post-chlorinated polyvinyl chloride. However since the post-chlorination considerably altered the properties of the polymer the requirement for pure, rigid polyvinyl chloride (free of plasticizers) continued to exist.

It has now been found that foam from rigid polyvinyl chloride of a very uniform, finely cellular quality can be obtained continuously by extrusion, if this extrusion takes place under the conditions to be specified in more detail hereinafter.

The invention can be defined as relating to a process for the continuous production of

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extruded foamed polyvinyl chloride containing not more than 5% by weight of plasticizer, comprising extruding a mixture of this polymer with a physical blowing agent, i.e. a liquid boiling below 100°C at normal pressure, whereby this mixture is pushed under pressure through a single shaft worm-screw extruder to a discharge orifice on leaving which the said liquid evaporates as a result of a sudden drop in pressure, the extruder comprising in sequence a mixing zone, a cooling zone and a discharge orifice, and the following conditions being observed: a) the said liquid is added to the polymer and mixed homogeneously therewith in the mixing zone, b) the temperature of the polymer just upstream of the mixing zone for polymer and liquid is between 170°C and 230°C and is between 80°C and 135°C at the downstream end of the discharge orifice, c) the pressure is at least 150 atm. abs. upstream of the mixing zone, and is at least 50 atm. abs. at the downstream end of the cooling zone and is at least 15 atm. abs. just upstream of the discharge orifice and d) the average residence time of the material between the initial entry point of the liquid and the downstream end of the said cooling zone is between 1 and 7 minutes.

The foam produced has the shape of rods (strands), pipes, profiles, films, plates and the like.

Apart from the plasticizer-free polymer the rigid types of polyvinyl chloride comprise also the mixtures thereof which have at most 5% by weight of the plasticizer based on the quantity of polymer. Plasticizers are compounds of very slight volatility, usually boiling above 200°C at 50 mm Hg. They are principally ester such as dioctylphthalate, dibutylphthalate, dioctyladipate, dioctylsebacate and tricresylphosphate.

A single shaft screw press or extruder is an apparatus in which the material is mechanically treated and pushed forward by means of only one continuous shaft on which screw blades and possibly projections which promote the mixing, are mounted. In the single shaft extruder used according to the process of the invention various sections can be distinguished.

At the beginning of the cylindrical space the thermoplastic material is supplied to the plasticizing zone. The screw causes the material to be moved forward whereby it is gradually heated to above the softening point and moreover becomes subject to pressure as a result of a gradual reduction in the space available to it. According to the invention the pressure created must be at least 150 atm. abs., and this condition is essential for the preparation of good quality foam. This pressure is as a rule also sufficient to drive the material through the further sections of the cylindrical space (where there are no screw

blades) to the discharge orifice. The part where the compression occurs is also known as the compression zone.

The plasticizing zone is followed by the mixing zone at the beginning of which the liquid which boils below 100°C at normal pressure, i.e. the physical blowing agent, is added. The mixing can be promoted in the mixing zone in various ways. Collars are often mounted on the shaft, so that the cross-sectional area available for transport of matter at the point of a collar is small in this zone. The collars are provided with axial or helical grooves. It is advantageous on each occasion to leave a space between two collars in which space the cross-sectional area available is larger than at the points occupied by the collars. A favourable pitch angle of the helical grooves in the collars is approximately 30° with respect to the screw shaft. Instead of a system of collars rounded projections are often mounted on the shaft to improve the mixing.

Instead of through one opening the physical blowing agent may be injected through two or more openings. These openings may be situated in one plane normal to the shaft of the extruder, and are preferably distributed in a symmetrical manner around the periphery of the cylinder. However these openings may also be arranged at different points in the longitudinal direction of the mixing zone. Naturally the mixing zone begins at the first opening through which physical blowing agent is injected.

The mixing zone is followed by the cooling zone in which the contact of the mixture with the cylinder wall which cools it at that point is promoted, usually by means of scrapers which pass along the cylinder wall. In the cooling zone the cooling, which has normally already commenced in the mixing zone, is intensified and in addition the mixing process is continued. The cooling zone terminates (by definition) at the point where the pressure drops to below 50 atm. abs. The end of the cooling zone is situated at the extrusion orifice if the pressure is still at least 50 atm. abs. just before this orifice. If however a lower pressure is used (for example a pressure between 15 and 30 atm. abs.) a choke is arranged upstream of the extrusion orifice, i.e. a restriction of the open cross-sectional area is effected, in such a way that at this choke a pressure drop occurs of from at least 50 atm. abs. to a lower pressure; in this case the cooling zone terminates (by definition) at this choke.

The temperatures which the material in the cylindrical space just upstream of the mixing zone attains are between 170°C and 230°C, preferably between 180°C and 210°C. Usually a drop in temperature occurs in the mixing zone. The average residence time of the thermoplastic material in the mixing zone

and the cooling zone together is, as already stated, between 1 and 7 minutes. The temperature limits just upstream of the mixing zone and the said average residence time are related to the extent that with a temperature of 170°C to 180°C a relatively long average residence time within the said time limits is recommended (approximately 5 to 7 minutes) and with a temperature of 210°C to 230°C a relatively short average residence time within the said time limits (1 to approximately 1.5 minutes) is recommended.

The average residence time is calculated from the volume of material supplied per unit of time and the volume of the mixing and cooling zones together.

For practical purposes the criterion of the average residence time can be replaced by a criterion relating to the length of mixing and cooling zones together. In the equipment suitable for the present invention this length may be at least 10 D and at most 25 D if D is equal to the diameter of the cylindrical space.

The conditions of pressure, temperature and residence time mentioned for the mixing and cooling zones are extremely closely associated with a good mixing, with avoidance of polymer decomposition; consequently these conditions are essential for the quality of the foam. In addition to the conditions laid down for the mixing and cooling zones there are other conditions which have direct reference to the extrusion itself. In this respect it has been found that a pressure of at least 15 atm. abs. just upstream of the extrusion orifice is essential also for the quality of the foam. Temperatures above 135°C at the end of the extrusion orifice would damage the uniformity of the foam. Temperatures which are too low at this point, in general below 80°C, result in a too slow evaporation of the blowing agent and are thus likewise unfavourable for the quality of the foam. In many cases temperatures at the end of the extrusion orifice of between 90°C and 110°C are very suitable.

The types of polyvinyl chloride which are most suitable for the extrusion of foam according to the invention have K-values (according to Fikenscher) of between 45 and 60. The most preferable are those having a K-value of at most 55. It is certainly possible in this manner to work entirely without the conventional plasticizers.

The physical blowing agents are as a rule ketones, esters or halogenated hydrocarbons. It is advisable to select the physical blowing agent and in this connection the temperature of the extruded material at the end of the extrusion orifice in such a way that this latter is at least 30°C above the boiling point at normal pressure of the physical blowing agent. Examples of suitable physical blowing agents are acetone, methyl formate, ethyl

formate, methyl acetate and mono- and dichloromethane. Mixtures of such compounds and in addition also solutions of carbon dioxide, for example in acetone, can also be used. The quantity of physical blowing agent is as a rule between 10 and 25% by weight, for example between 12 and 18% by weight, based on the quantity of the thermoplastic material.

The uniformity of the foam formation is further promoted by the presence of a nucleating agent; nucleating agents are finely divided solid substances, such as zinc silicate or calcium silicate, silica and bentonite, with a particle size of at least 100 microns, or other substances or mixtures of substances which evolve a gas by means of a chemical reaction (chemical blowing agents). Preference is given to a mixture of an organic acid, such as citric acid, malonic acid or phthalic acid, with a carbonate or bicarbonate. In addition nitrogen-evolving compounds such as azodicarbonamide can be used as nucleating chemical blowing agent. Usually the nucleating agent is used in quantities not greater than 1 to 2% by weight, based on the quantity of polymer.

In addition to the additives mentioned above the foam-forming compositions normally also contain stabilizers and often lubricants, pigments or dyes. Stabilizers counteract the decomposition of the polyvinyl chloride. Suitable stabilizers are for example tribasic lead sulphate and dibasic lead stearate. Many other compounds which are cited in the literature as stabilizers for polyvinyl chloride are likewise very suitable for use. In general stabilizers are used in quantities of at most 5% by weight, based on the quantity of polymer. Suitable lubricants are for instance calcium laurate, calcium stearate, glycerol monostearate and triethylene glycol; many other lubricants however are also suitable, and in this context reference can again be made to the relevant literature.

The diameter of the cells present in the foam and the density of the foam are dependent on the nature and quantity of physical blowing agent and nucleating agent and on the rate of extrusion.

It has been found possible according to the invention to prepare uniform foams having average cell diameters between 0.2 and 4 mm and densities between 0.01 and 0.5 g/ml. Vinyl chloride foams having an average cell diameter of less than 0.5 mm and at the same time a density of below 0.3 g/ml cannot be obtained in any other way than by the process according to the invention and are novel products. Foams having a density of between 0.01 and 0.03 g/ml are particularly interesting.

Foams of densities and average cell diameter that can be made by processes known in the art can be made more advantageously

in accordance with the present invention, since the conventional processes are discontinuous and cumbersome and expensive due to their equipment and requirement of expensive chemical blowing agents.

The foams according to the invention are excellently suited for use as weather and chemical resistant heat- and sound-insulating materials. They are difficultly flammable and self extinguishing and do not drip on being directly heated. These properties make them particularly suitable for use in the building industry.

By way of example the accompanying drawing shows diagrammatically an apparatus suitable for carrying out the present process. The cylindrical barrel or shell of the extruder is drawn in vertical cross-section, while the screw on the other hand is shown in elevation.

The barrel is provided with a feed hopper 1 for the supply of polymer and an opening 2 for the supply of physical blowing agent. At the end is an extrusion die head 3 (in cross-section) with a choke 4 and an extrusion orifice 5.

The space is divided into a plasticizing zone 6, a mixing zone 7 and the cooling zone 8. This latter zone finishes in the present case at the choke 4.

A rotating shaft 9 in the plasticizing zone

6 has a diameter which increases gradually in the direction of movement and which provides compression. In the plasticizing zone 6 worm-screw blades 10 are also mounted on the shaft 9.

Upstream of the mixing zone a throttle 11, is situated on the shaft 9, the diameter of which throttle differs very little from the inside diameter of the barrel and which prevents the physical blowing agent from flowing upstream. Collars 12 having helical grooves are arranged in the mixing zone 7 on the shaft 9. In each case between two collars a space 13 is present in which the forces exerted on the propelled mass are smaller than at the points occupied by the collars.

In the cooling zone 8 the rotating shaft which is here cylindrical carries two scraping elements 14 one of which is visible.

The scraping elements comprise a number of scraping blades 15 which make an oblique angle with the shaft and which move closely over the inner wall of the shell. Between the blades 15 are openings 16 into which the mass to be extruded can pass.

The barrel or shell and sometimes also the shaft contain heating and cooling elements which can be switched on as and when required.

By way of example suitable dimensions are the following:

Inside diameter of the barrel D	=60 mm
Length of the plasticizing zone	=13 D to 20 D
" throttle 11	= $\frac{1}{2}$ D
" mixing zone	=10 D
" cooling zone	=5 D

Distance from the rotating shaft to the cylinder barrel at the downstream end of the plasticizing zone=3.5 mm

Diameter of the throttle 11=59.6 mm

Depth of the grooves in the collars 12=3 mm

Diameter of the rotating shaft in the cooling zone=40 mm

Diameter of the opening in the choke 4=4 mm

Length of the opening 4 (in the direction of the movement)=20 mm

Diameter of the extrusion orifice 5=8 mm

Length of the extrusion orifice 5 (in the direction of movement)=40 mm

EXAMPLE I

The following mixture was introduced into the extruder through the hopper 1 (parts by weight):

polyvinyl chloride (K=55) in powder form	100
tribasic lead sulphate	4
calcium stearate	1
triethylene glycol	1.5
glycerol monostearate	1.5
sodium bicarbonate	0.1
citric acid	0.08

The dimensions of the apparatus were those given by way of example above; the actual length of the plasticizing zone was 16 D. There were heating and cooling elements in the barrel but not in the shaft. The compression ratio in the plasticizing zone was 1:3.3.

The physical blowing agent was acetone used in a quantity of 15% by weight based on the quantity of polyvinyl chloride.

The screw shaft rotated at 35 r.p.m.

The following temperatures were maintained in the barrel.

Along the plasticizing zone at 4 measuring points in the direction of movement; 130, 170, 195 and 215°C.

Along the mixing zone a temperature gradient from 160°C to 80°C.

In the cooling zone: 60°C.

The temperature of the polymer at the end of the plasticizing zone was 200°C. The temperature of the material at the extrusion orifice (i.e. the temperature of the material which had just left the extrusion orifice) was 115°C.

The average residence time of the material in the mixing and cooling zones together was 122 seconds.

The pressure distribution was as follows:
in front of the throttle: 305 atm. abs.

at the acetone injection point: 220 atm. abs.

5 at the end of the rotating shaft: 70 atm. abs.

in front of the extrusion orifice 5: 20 atm. abs.

10 A homogeneous foam was obtained in the form of a smooth strand with a yield of 27 kg/hr. The density was 90 g/l and the cell diameter 1.0 to 1.2 mm.

EXAMPLE II

15 The starting material was the same as in Example I but the polyvinyl chloride was also mixed with 5% by weight of dioctyl phthalate.

The course of the extrusion was similar to that described in Example I but the pressures were:

20 in front of the throttle: 290 atm. abs.

at the acetone injection point: 205 atm. abs.

at the end of the rotating shaft: 55 atm. abs.

25 in front of the extrusion orifice 5: 15 atm. abs.

A homogeneous foam was obtained in a yield of 25 kg/hr.

EXAMPLE III

30 The starting material was the same as in Example I but the quantity of sodium bicarbonate and citric acid used was 5 times as large. Under the same conditions as described in Example I a foam was obtained having a very fine cell structure. The average cell diameter was 0.25 mm and the density 80 g/l.

EXAMPLE IV

40 The starting material and the conditions were as described in Example 1 with the exception that instead of acetone, monochloromethane was used. The foam had a density of only 16 g/l and an average cell diameter of 0.4 mm.

45 WHAT WE CLAIM IS:—

1. A process for the continuous production of extruded foamed polyvinyl chloride containing at most 5% by weight of plasticizer, comprising extruding a mixture of this polymer with a physical blowing agent, i.e. a liquid boiling below 100°C at normal pressure, whereby this mixture is pushed under pressure through a single shaft worm-screw extruder to a discharge orifice on leaving which the said liquid evaporates as a result of a sudden drop in pressure, the extruder comprising in sequence a mixing zone, a cooling zone, and a discharge orifice, and the following conditions being observed: a) the said liquid is added to the polymer and

mixed homogeneously therewith in the mixing zone, b) the temperature of the polymer just upstream of the mixing zone for polymer and liquid is between 170°C and 230°C and is between 80°C and 135°C at the downstream end of the discharge orifice, c) the pressure is at least 150 atm. abs. upstream of the mixing zone and is at least 50 atm. abs. at the downstream end of the cooling zone and is at least 15 atm. abs. just upstream of the discharge orifice and d) the average residence time of the material between the initial entry point of the liquid and the downstream end of the said cooling zone is between 1 and 7 minutes.

2. A process as claimed in claim 1, in which the length of the extruder between the initial entry point of the liquid and a choke upstream of the discharge orifice is 10 times the inside diameter of the barrel or shell of the extruder at that point.

3. A process as claimed in claim 1 or 2, in which use is made of polyvinyl chloride having a k-value of at most 60.

4. A process as claimed in any of claims 1—3, in which the temperature of the polymer just upstream of the mixing zone is between 180°C and 210°C.

5. A process as claimed in any of claims 1—4, in which use is made of polyvinyl chloride without a plasticizer.

6. A process as claimed in any of claims 1—5, in which the physical blowing agent is a ketone, an ester or a halogenated hydrocarbon.

7. A process as claimed in any of claims 1—6, in which the amount of physical blowing agent is between 10 and 25% by weight, based on the quantity of the polymer.

8. A process as claimed in any of claims 1—7, in which a nucleating agent is added to the polymer before mixing the physical blowing agent.

9. A process as claimed in claim 8, in which the nucleating agent is a mixture of a carbonate and/or a bicarbonate with an organic acid.

10. A process as claimed in claim 1 substantially as described with reference to the accompanying drawings.

11. A process as claimed in claim 1 substantially as described in any of the Examples.

12. An extruded foamed product of polyvinyl chloride, whenever produced according to any of claims 1—11.

13. An extruded foamed product of polyvinyl chloride, having a density less than 0.3 g/ml and an average cell diameter less than 0.05 cm.

14. A foamed product as claimed in claim 13, having a density between 0.01 and 0.03 g/ml.

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15. Articles whenever completely or partially produced from foamed products as claimed in claims 12—14.

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1137339 COMPLETE SPECIFICATION

1 SHEET. *This drawing is a reproduction of the Original on a reduced scale*

